



Influence of fumed silica and additives on the gel formation and performance of gel valve-regulated lead-acid batteries

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ABSTRACT

The gel electrolyte is an important factor that controls both the manufacturing process and the performance of gel valve-regulated lead-acid (gel VRLA) batteries. In this study, the influence of the concentration of fumed silica and four additives in the gel electrolyte formulation on the gelling process, electrochemical behavior and battery performance was investigated. Higher fumed silica concentrations and the presence of polyacrylamide and vaniline led to a shorter gelling time and a firmer gel. Of the gel formulations studied, gel VRLA batteries with or without 0.005% (w/v) vaniline had a higher discharge capacity than the conventional liquid VRLA battery.

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1. Introduction

Lead-acid batteries are an important and commonly used component in the storage and transport of renewable energy, such as solar energy. They are one of the most practical and widely used secondary batteries to store energy due to their low cost, ruggedness, high reliability and ability to supply high surge currents, despite their having a relatively very low weight and volume energy densities. Conventional lead-acid batteries consist of negative and positive plates, which are made of lead and lead dioxide, respectively, immersed in a liquid sulfuric acid electrolyte, and are generally called “flooded lead-acid batteries”. Due to their simple design, they allow hydrogen and oxygen gases created during the charge cycle to vent to the atmosphere so that distilled water must be regularly added to maintain the electrolyte level and sulfuric acid concentration. Accordingly, they require regular maintenance. To minimize the battery water loss and so eliminate (or reduce) the need for regular attention for maintenance, “valve-regulated lead-acid (VRLA) batteries” have been developed [1].

VRLA batteries are sealed lead-acid batteries, which have pressure-release valves to allow the gases to escape when the

internal pressure exceeds a certain level. They are designed to have an immobilized electrolyte so that oxygen generated during the charge cycle is captured and recombined in the battery, a so called “oxygen recombination cycle”, leading to less or no water loss. Although several reports have shown that conventional flooded lead-acid batteries have higher capacities than VRLA batteries [2,3], VRLA batteries have gained interest in the last two decades but still require a significant improvement in their performance [1–15]. There are two techniques to immobilize the electrolyte in the VRLA batteries. In the first method the liquid sulfuric acid electrolyte is captured in an absorptive glass mat (AGM) separator, whilst in the second method the sulfuric acid solution is gellified by a gelling agent to form a gelled sulfuric electrolyte. The advantages of having a gelled sulfuric electrolyte are the lower corrosion problems, due to no or less leakage of acid electrolyte, and the flexibility of being able to install the battery in any orientation.

One of the key factors that affect the performance of gel VRLA batteries is the gelled electrolyte itself. The properties of the gelled electrolyte, such as the gel strength and rheology, can be influenced by various factors during the gel preparation, such as the concentration of the sulfuric solution and the type and concentration of gelling agents. The properties of the gelled electrolyte then, in turn, affect the electrolyte filling process and, ultimately, the performance of the gel VRLA batteries. If the electrolyte forms a gel too fast and gels before the filling process is finished, the gelled electrolyte is not distributed throughout the

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entire cell and air voids are created in the battery cells, which results in a poor battery performance. On the other hand, if the electrolyte forms a gel too slowly then the throughput efficiency of the battery manufacturing process is reduced and becomes economically unviable.

This work studied the preparation of gel electrolytes for use in VRLA batteries, where the effect of different fumed silica concentrations and that of different additives on the gelling process, on the electrochemical behavior and on the performance of the VRLA batteries were investigated. The performance test of the batteries was performed under 100% depth of discharge (100% DoD) conditions. Poly(methyl methacrylate) (PMMA), polypyrrole (PPY), polyacrylamide (PAM) and vaniline (VA), a benzaldehyde derivative, were used as the additives in this study. The rationale for the choice of these four additives was based upon their known previous usage. That is PAM has been reported as an additive in the preparation of gelled electrolytes for VRLA batteries [4], PMMA has been used to form the gelled electrolyte for rechargeable lithium batteries due to its high conductivities and good electrochemical stability [16–18], while benzaldehyde derivatives, such as veratraldehyde, have been reported to inhibit the hydrogen evolution reaction and reduce the water loss in flooded lead-acid batteries [19]. Finally, PPY was included in this study to see if a conductive polymer had any influence on the performance of the lead-acid batteries.

2. Experimental

Electrolytes were prepared with sulfuric acid (1.325 g cm^{-3}) (Qrec), sodium sulfate (0.013 g cm^{-3}) (Ajax Finechempy) and various amounts (3–6%, w/v) of fumed silica (SiO_2). To investigate the effect of additives, different amounts of the four additives (PMMA (MW = 15×10^3) (Aldrich), PPY (Aldrich), PAM (MW = 6×10^6) (Aldrich) and VA (Aldrich)) were added to the electrolytes and mixed at 2000 rpm for 10 min.

The gelling process was investigated by evaluation of the gelling time and the gel characteristics during and after the electrolyte filling process. The gelling times of the electrolyte formulations were obtained by measuring the penetration of 3-mm diameter lead balls when dropped into the electrolyte at different times from a constant height above the gel surface (2 cm). Those gelled electrolyte formulas having suitable gelling times (longer than 3 h) were then selected to fill into the 12 V/4 Ah AGM VRLA batteries under a vacuum condition. Only the gelled electrolyte formulations that still maintained a liquid state until all the electrolyte was completely distributed throughout the battery cells were chosen for subsequent examination of their electrochemical behavior and battery performance.

To investigate the electrochemical behavior of the gel formulations, cyclic voltammetry experiments were carried out on the gelled electrolytes after they had been left for 5 days to assure complete gel formation. A three-electrode cell, consisting of a 0.5-cm^2 planar lead working electrode, a platinum gauze counter electrode and a Ag/AgCl reference electrode, was used for electrochemical testing. All potentials reported herein correspond to the Ag/AgCl scale. Prior to each experiment, the lead working electrode was polished with SiC-type abrasive papers (800, 1500 and 2000 grades sequentially). Cyclic voltammetry was conducted between -2.5 and 3.0 V vs. Ag/AgCl at a 50 mV s^{-1} scan rate using an Autolab PGSTAT potentiostat (Eco Chemie).

To compare the performance of the batteries, the 12 V/4 Ah AGM VRLA batteries filled with the selected electrolyte formulations were tested based on the JIS standard [20] under 100% DoD at a low-rate discharge (0.1 C) and, in particular cases, at a high-rate discharge (1 C) using an Ultimate Battery Analyzer (UBA4) instrument (Vencon Technologies) and a battery charge/discharge

Table 1

Cyclic test algorithms used in the battery tests under a 100% depth of discharge (DoD).

Step	100% DoD	
	Low-rate discharge (0.1 C)	High-rate discharge (1 C)
1	Charge (0.8 A/14.1 V/7 h)	Charge (1 A/14.1 V/9 h)
2	Rest (5 h)	Rest (5 h)
3	Discharge (0.4 A/10.5 V)	Discharge (4 A/9.6 V)
4	Charge (0.8 A/14.1 V/11 h)	Charge (1 A/14.1 V/9 h)
5	Repeat steps 3 and 4 14 times ^a	Repeat steps 3 and 4 29 times

^a For the self-discharge test: repeat five times.

and data processing control system (Huizhou Xinkehua Industry), respectively. The cyclic testing algorithms for the battery tests are shown in Table 1. After the tests, the selected batteries were carefully disassembled to investigate the physical structure of the negative plates using scanning electron microscopy (SEM) (JEOL JSM-6400), whilst X-ray diffraction analysis (XRD) (Bruker D8-Discovery) was used to examine the phase compositions of the negative plates. The self-discharge of VRLA batteries was investigated by monitoring the voltage of the batteries (i.e., open circuit voltage test) every week for three months and then testing the batteries under 100% DoD at a low-rate discharge (0.1 C). The gelled electrolyte formulation containing veratraldehyde (Aldrich), which has been studied previously [21], was also included in the self-discharge study for comparison. All electrochemical experiments were conducted at room temperature ($30 \pm 3^\circ \text{C}$).

3. Results and discussion

3.1. Gel characteristics

With the aim of forming improved gelled electrolytes that are suitable for use in VRLA batteries, the gel characteristics, including the stability, strength and gelling time, are crucial, especially during the electrolyte filling process. The penetration of the dropped lead balls into the different gel electrolytes (the surrogate measure of gel firmness and strength) at different times is shown in Fig. 1. As the SiO_2 concentration was increased from 3 to 4% (w/v) no significant difference was noted but when increased to 5 and especially to 6% (w/v) the gelling time was reduced and the gel strength increased (Fig. 1a). The electrolytes prepared with 3 or 4% (w/v) SiO_2 took more than 5 h to form a gel, whilst those prepared with 5 and 6% (w/v) SiO_2 started to form a gel after 3 and 2 h, respectively. It is likely that the higher SiO_2 concentration led to the formation of a greater silanol-bonding network (i.e., the network of Si–O–H through the hydrogen bridge linkages), which then resulted in a faster and firmer gelled electrolyte. It should be noted that if the electrolyte forms a gel too fast or forms a gel before all the electrolyte solution has been distributed throughout the battery cell, then trapped air zones can be created in the battery cells that lead to a poor battery performance. On the other hand, if the electrolyte is too soft or does not have a good stability, a good gel structure may not be formed. The gelled electrolytes prepared with 6% (w/v) and higher (not shown) SiO_2 gelled too fast and so were excluded from further analysis, while those prepared from 4 and 5% (w/v) SiO_2 were chosen for further study with the addition of 0.5% (w/v) of each of the four different additives.

With 5% (w/v) SiO_2 , the addition of 0.5% (w/v) PPY or PMMA did not reveal any substantial change in the gelling time (Fig. 1b). In contrast, the addition of 0.5% (w/v) of either PAM or VA significantly shortened the gelling time such that the electrolyte almost formed a firm gel state immediately (Fig. 1b). To further investigate the gel formation in samples prepared with the inclusion of PAM or VA, the amount of each additive was decreased

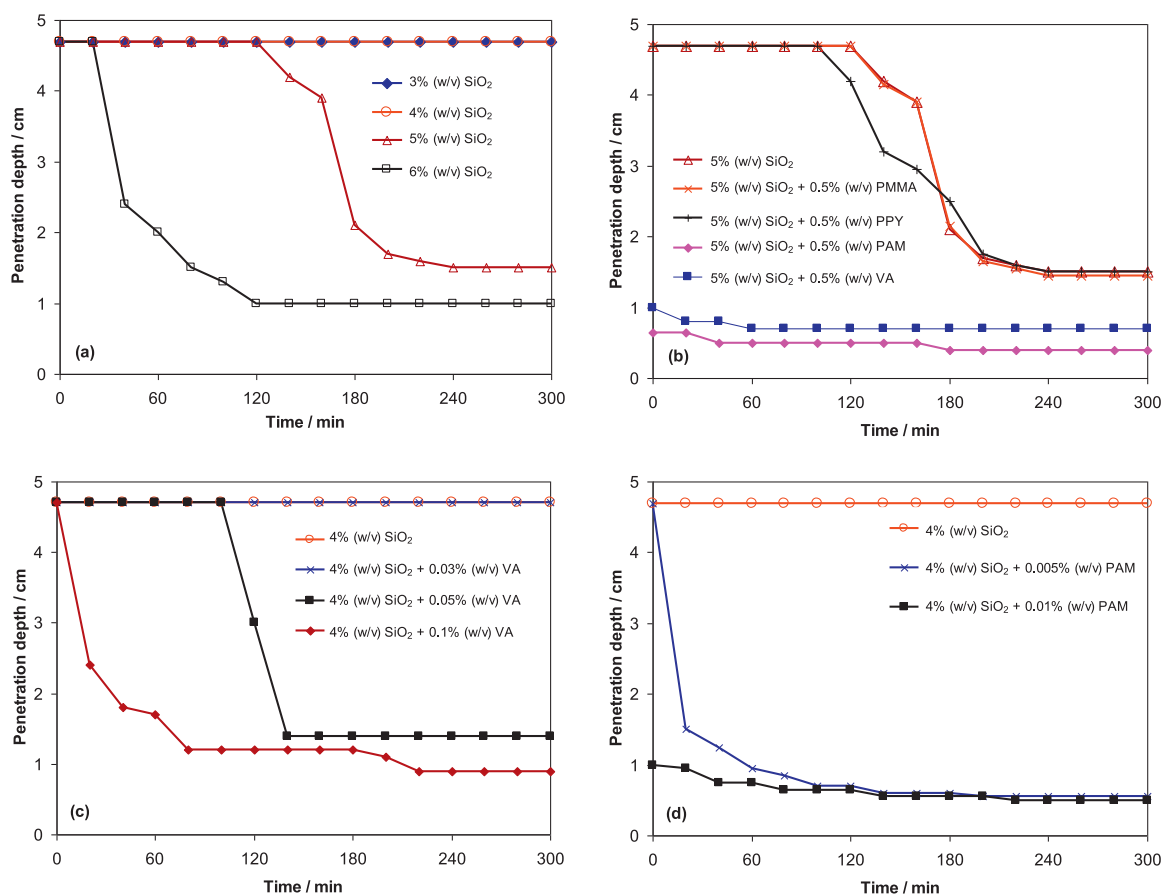


Fig. 1. Penetration depth of lead balls dropped from 2 cm above the gel surface at different times in gelled electrolytes with (a) different SiO₂ concentrations, (b) 5% (w/v) SiO₂ and different additives at 0.5% (w/v), (c) 4% (w/v) SiO₂ and different VA concentrations and (d) 4% (w/v) SiO₂ and different PAM concentrations.

to below 0.5% (w/v) with a fixed concentration of 4% (w/v) SiO₂. Lowering the VA concentration led to a longer gelling time, but a VA concentration of 0.1% (w/v) still resulted in too fast a gelling process (Fig. 1c). In the presence of PAM, even at a concentration of only 0.005% (w/v), the electrolytes formed a gel state almost immediately and gel formation was firm before 1 h and complete by 2 h (Fig. 1d). This very short gelling time for the electrolytes prepared with PAM was likely to be due to the enhancement of the gel network formation attributed from bridge formation between the nitrogen in the polyacrylamide side group and the silica particles [22].

Only gel electrolyte formulations that had a gelling time of longer than 3 h were selected for the further evaluation since they were less viscous and would allow the electrolyte to be completely distributed throughout the battery cells with few or no air voids. Therefore, PAM as an additive was excluded in this study, despite the fact that it has been reported previously to be of its use in preparing gelled electrolytes [4].

3.2. Electrochemical studies

The cyclic voltammograms obtained for the lead electrodes in the liquid and the different gelled electrolytes are shown in Fig. 2. No additional peaks appeared in the voltammograms of any of the different gel formulations, that is those with the addition of SiO₂ at 4 or 5% (w/v) alone or with the addition of any of the three additives into the gelled electrolytes. Rather, only peaks at −0.5 V and 1.5 V, which correspond to the reactions of Pb/PbSO₄ and PbO₂/PbSO₄ [23,24], respectively, were observed, which was the same as that seen with the liquid electrolyte. Since there was no

secondary redox reaction from the SiO₂ or the three additives, then these gelled electrolyte formulations potentially should be able to be used in lead-acid batteries. The gelled electrolytes revealed lower hydrogen and oxygen reaction rates than the liquid electrolyte, presumably due to the limitation of ion diffusion imposed by the three-dimensional network structure of the gel [21]. The addition of PMMA and PPY did not show any substantial effect on electrochemical behaviors (Fig. 2a and b). On the other hand, the presence of VA resulted in much lower hydrogen and oxygen evolution rates compared to that from the corresponding 4% (w/v) SiO₂ gelled electrolyte without any additive (Fig. 2c), despite their being no detectable shift in the hydrogen and oxygen overpotentials. This would likely result in a lower water loss and longer service life for the gelled electrolyte batteries. In addition, increasing the concentration of VA resulted in the reduction in the hydrogen and oxygen evolution rates in a dose-dependent manner, which is similar to that previously reported for the addition of veratraldehyde [21]. This is not surprising since they are both benzaldehyde derivatives.

3.3. Battery test

The discharge capacities and discharge times under a 100% DoD at a low-rate discharge (0.1 C) of the gel VRLA batteries prepared with 4 or 5% (w/v) SiO₂ and different additives are shown in Fig. 3, while representative SEM images and some XRD results of the negative plates of the VRLA batteries after the 100% DoD test are shown in Figs. 4 and 5, respectively. The discharge capacity of the conventional liquid AGM VRLA battery is also included in Fig. 3 for comparison. The liquid AGM VRLA battery had a very high initial

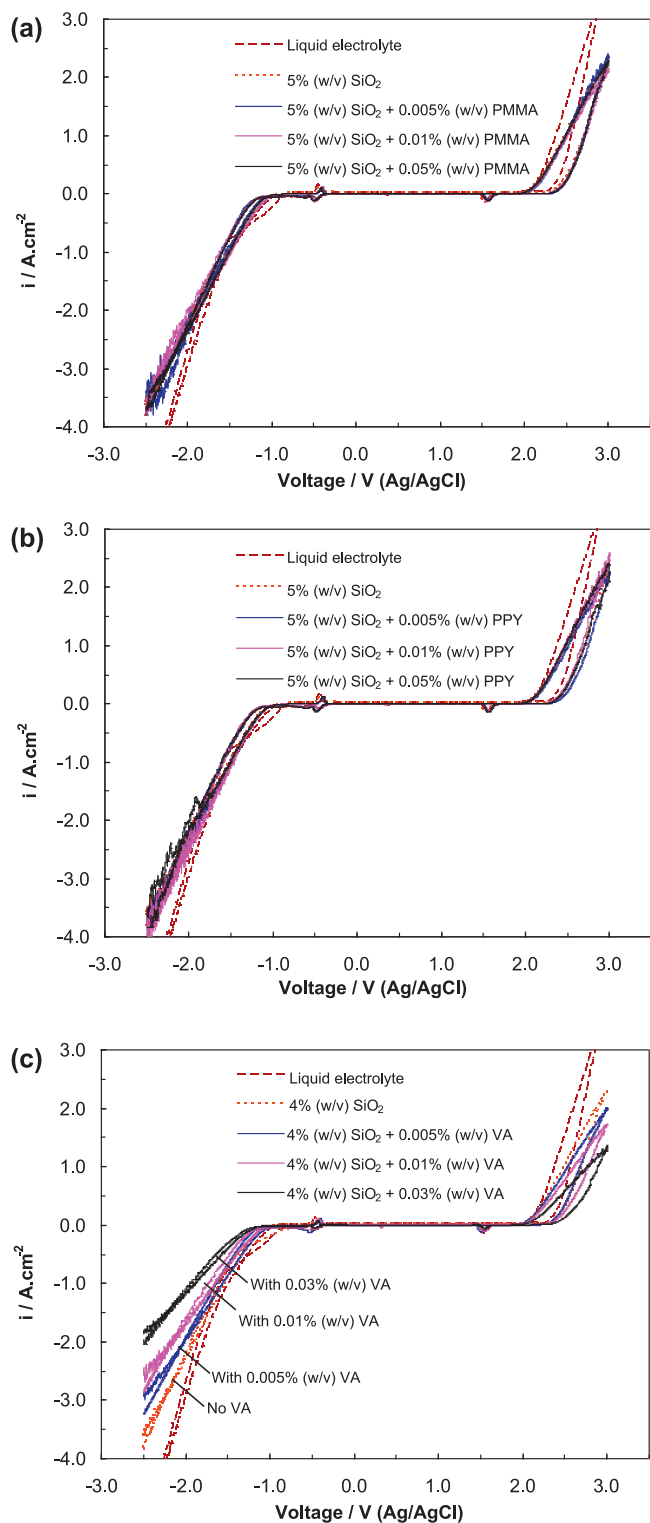


Fig. 2. Cyclic voltammograms of the lead working electrodes in the different electrolytes at 50 mV s^{-1} . Shown are gelled electrolytes with 5% (w/v) SiO_2 with different (a) PMMA or (b) PPY concentrations, and (c) with 4% (w/v) SiO_2 and different VA concentrations.

discharge capacity compared to the different gel VRLA batteries, but as the charge/discharge process continued, its discharge capacity decreased sharply, especially in the first eight cycles (Fig. 3). In most cases, the discharge capacities of the gel VRLA batteries were very low in the first cycle and then gradually increased and remained stable throughout the remaining test

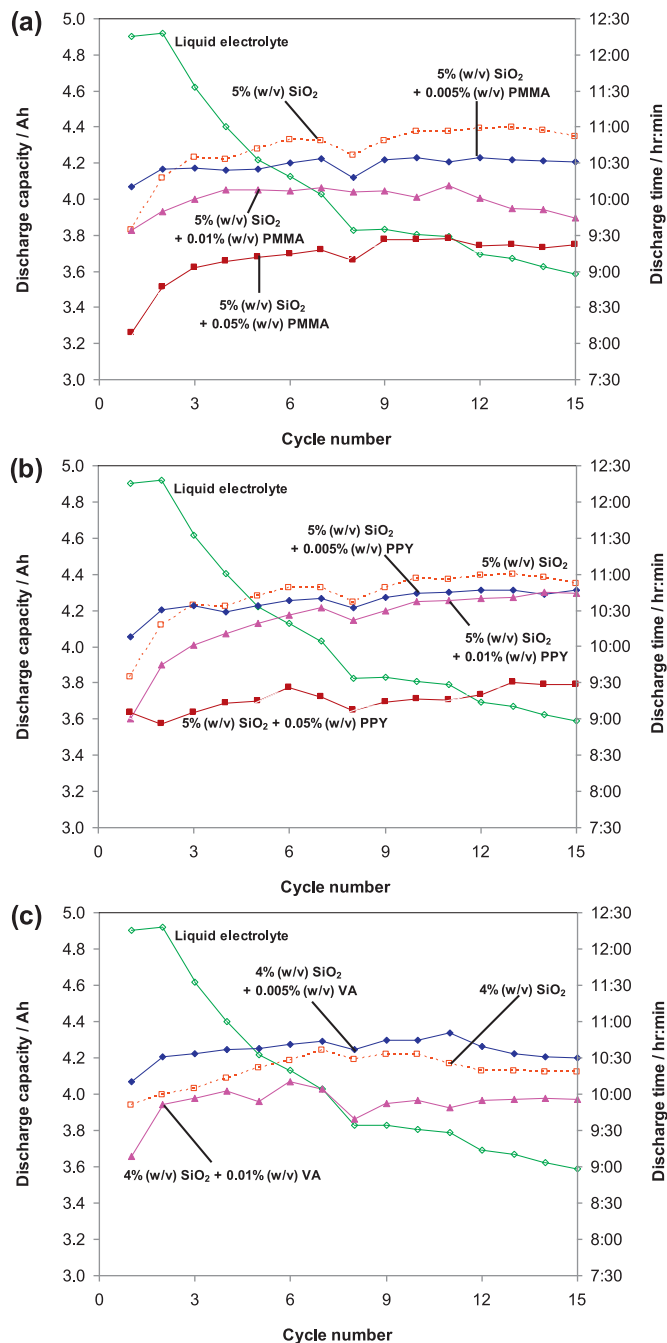


Fig. 3. Discharge capacities and discharge times of gel VRLA batteries prepared with different electrolytes during 100% DoD tests at a low-rate discharge (0.1 C). Shown are (a, b) 5% (w/v) SiO_2 gelled electrolytes with different (a) PMMA or (b) PPY concentrations, and (c) with 4% (w/v) SiO_2 gelled electrolytes and different VA concentrations.

period. The gradual increase in the observed discharge capacity of the respective gel VRLA batteries with increasing numbers of discharge cycles may be attributed to the better distribution of the gelled electrolyte throughout the battery cells during the first few charge/discharge cycles due to the thixotropic properties of the gelled electrolytes [2]. Fig. 3a and b indicates that the addition of PMMA or PPY reduced the battery performance in a dose-dependent manner as the amount of these additives was increased from 0.005 to 0.01% (w/v). On the other hand, the performance of the gel VRLA battery was enhanced by the addition of VA at 0.005% (w/v) (Fig. 3c), but decreased at the higher VA level of 0.01% (w/v).

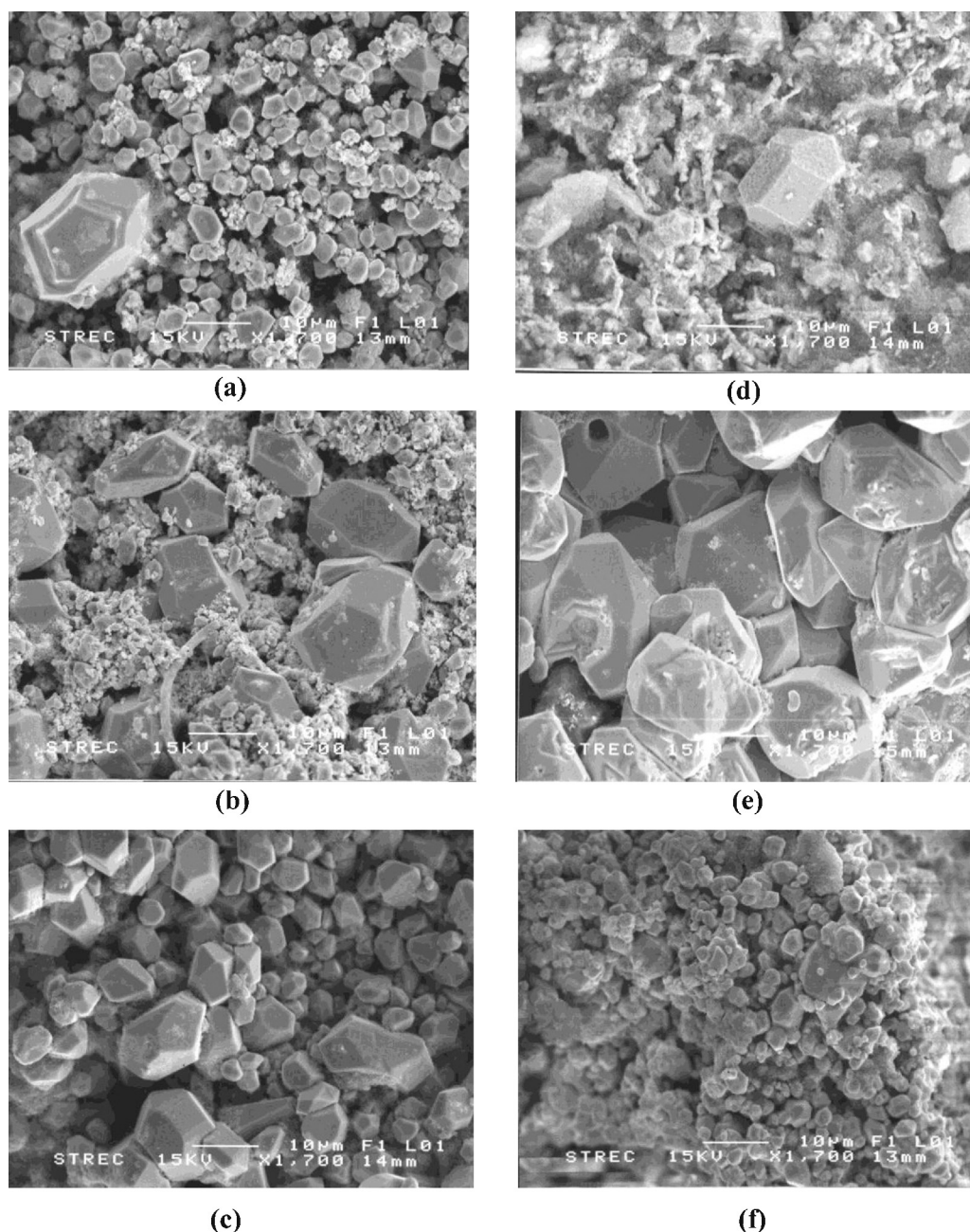


Fig. 4. SEM images (all at 1700 $\times$ magnification) of the negative plates from gel VRLA batteries with different gelled electrolytes (a) gelled electrolyte with 5% (w/v) SiO_2 and 0.005% (w/v) PMMA, (b) gelled electrolyte with 5% (w/v) SiO_2 and 0.005% (w/v) PPY, (c) gelled electrolyte with 5% (w/v) SiO_2 having no additive, (d) gelled electrolyte with 4% (w/v) SiO_2 and 0.005% (w/v) VA and (e) gelled electrolyte with 4% (w/v) SiO_2 and 0.01% (w/v) VA, (f) gelled electrolyte with 4% (w/v) SiO_2 having no additive, after 100% DoD tests at the low-rate discharge (0.1 C).

Based on the cyclic voltammograms for PMMA (Fig. 2a) and PPY (Fig. 2b), their addition was not expected to effect the electrochemical reactions taking place during the battery operation, and so they were neither expected to improve nor to deteriorate the battery performance. It is, at this point, then still difficult to precisely explain how the addition of PMMA or PPY deteriorated the battery performance. It is possible that the addition of these two additives at levels even as low as 0.005% (w/v) may affect the structure of the electrodes or may increase the sulfation rate, as big polyhedral crystals of lead sulfate were formed (Fig. 4a and b vs. Fig. 4c). The formation of lead sulfate crystals during battery operation is an irreversible process and deteriorates the performance of the battery [1]. In addition, the XRD results revealed the presence of lead oxide sulfate hydrate (i.e., $(\text{PbO})_3(\text{Pb}(\text{SO}_4))(\text{H}_2\text{O})$),

in addition to lead sulfate crystals, on the negative plates of the gel VRLA battery with PMMA and PPY (Fig. 5a–c). Accordingly the decreased battery performance in the presence of PMMA or PPY in the electrolyte may also be due to the formation of lead oxide sulfate hydrate.

Unlike the addition of PMMA or PPY, the addition of VA may suppress the hydrogen and oxygen evolution (Fig. 2c), and so may reduce the water loss during the battery operation. However, like the addition of PMMA or PPY, the addition of VA also led to the formation of lead oxide sulfate hydrate on the negative plate of the gel VRLA battery (Fig. 5d). In addition, the presence of VA in the gel electrolyte was observed to alter the morphology of the electrodes during the battery operation, but in an opposite manner depending on the amount of VA added (Fig. 4d and e vs. Fig. 4f). Overall, the

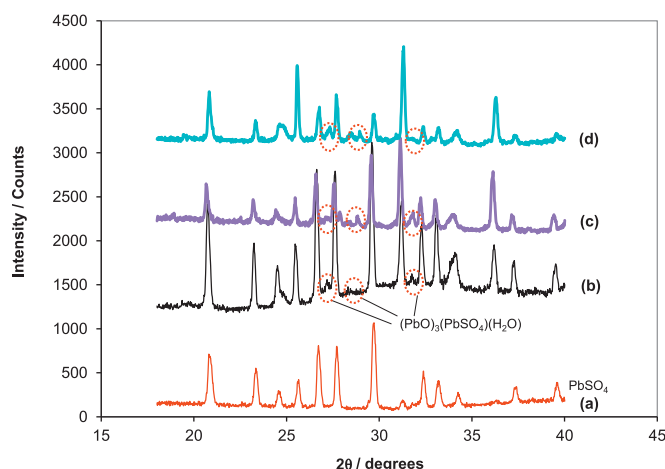


Fig. 5. XRD patterns of negative plates from 12 V/4 Ah AGM VRLA batteries (after 100% DoD tests at a low-rate discharge (0.1 C)) with a 4% (w/v) SiO_2 gelled electrolyte with (a) no addition, (b) 0.005% (w/v) PMMA, (c) 0.005% (w/v) PPY, and (d) 0.005% (w/v) VA.

negative plate of the gel VRLA battery with 0.005% (w/v) VA had a finer structure (Fig. 4d) compared to that without VA (Fig. 4f), whereas increasing the VA concentration to 0.01% (w/v) enhanced the sulfation process and resulted in much larger lead sulfate crystals (Fig. 4e). The relative level of these three effects may counteract or enhance one and another leading to the improved or deteriorated performance of the battery depending on the amount of VA added.

At a low VA concentration (0.005% (w/v)), the suppression of the hydrogen and oxygen evolution may have elicited a stronger effect than the deteriorating effect due to the formation of lead oxide sulfate hydrate, and so overall results in an improved battery performance. On the other hand, at the higher VA concentration (0.01% (w/v)), despite a higher suppression of the hydrogen and oxygen evolution rates (Fig. 2c), the formation of lead oxide sulfate hydrate and the much larger lead sulfate crystals dominate and so overall a significantly lower discharge capacity was obtained than that with the gel VRLA batteries prepared without any VA or with only 0.005% (w/v) VA (Fig. 3c). A somewhat similar trend in the results was seen in the case of a 100% DoD at a high-rate (1 C) discharge (Fig. 6). The observed discharge capacities at both a low- and a high-rate discharge indicated that high VA concentrations (0.01% (w/v)) deteriorated the battery performance. From these results it appears that the influence of VA upon the hydrogen and

oxygen evolution rates was unlikely to be the only significant factor dictating the battery performance.

3.4. Self-discharge test

Normally, batteries are not used immediately after their manufacture, but are left on the distribution and retail shelves for several months before being used. Although these batteries have not been connected to an external load, the capacity of the batteries continues to decrease since the batteries can discharge on their own. This self-discharge is caused by electrochemical processes within the cell and is equivalent to applying a small external load. Good batteries then would have the ability to preserve a high charge capacity during their shelf-period. Flooded lead-acid batteries typically have a high self-discharge rate compared to VRLA batteries since the antimony in the electrodes (added to increase their mechanical strength) increases the self-discharge rate. The self-discharge rate for a given design of VRLA battery is expected to depend on several factors that include the electrolyte composition. The residual capacity of the VRLA batteries with selected electrolytes over three months is shown in Fig. 7, while the subsequent discharge capacity of these batteries under a 100% DoD at a low-rate discharge (0.1 C) after the three month shelf-period is shown in Fig. 8.

The liquid VRLA battery tended to decay with storage, with its remaining discharge capacity dropping some 7% in the first week of storage and thereafter declining fairly steadily to ~88% remaining capacity after 11–12 weeks storage (Fig. 7). On the other hand, the gel VRLA batteries still retained their full capacities for at least five weeks before declining thereafter to a 93–95% remaining capacity after 12 weeks of storage. After the three-month storage period the discharge capacities of the 4% (w/v) SiO_2 gel VRLA batteries with and without 0.005% (w/v) veratraldehyde, a benzaldehyde derivative used in the previous study [21], were very similar to each other over the 6 sequential discharge cycles, and were all high being at around 4.1 Ah (Fig. 8). Indeed, these discharge capacities were very similar to that seen for the gel VRLA batteries without additives prior to storage (Fig. 3c). In contrast, the discharge capacity after the three month shelf-period of the gel VRLA battery prepared with 0.005% (w/v) VA was, however, significantly lower than those prepared without any additive or with 0.005% (w/v) veratraldehyde and was somewhat similar to that seen for the liquid VRLA battery. It is worth noting that there was no evidence of lead oxide sulfate hydrate formation on the negative plate of the gel VRLA battery without any additive (Fig. 5a) or with 0.005% (w/v) veratraldehyde [21] after the 100% DoD test. Thus, the lead

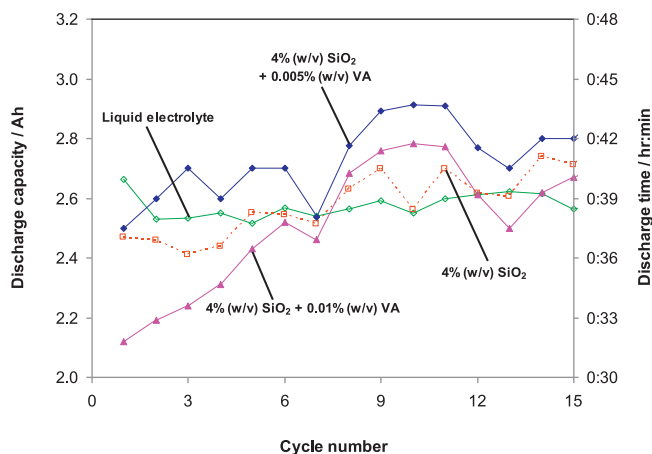


Fig. 6. Discharge capacities and discharge times of VRLA batteries prepared with different electrolytes during 100% DoD tests at the high-rate discharge (1 C).

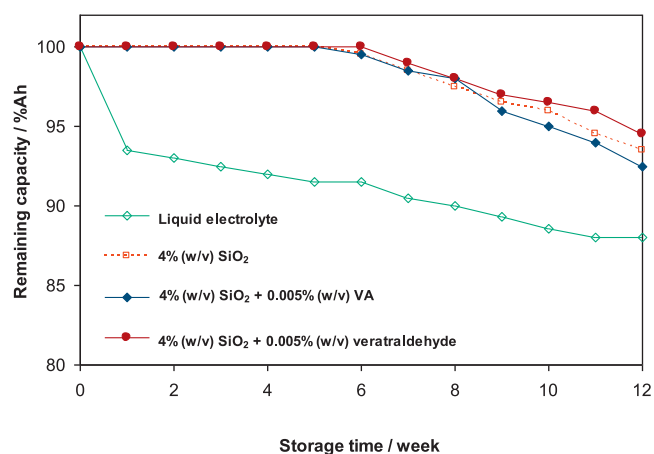


Fig. 7. Remaining capacities of VRLA batteries prepared with different electrolytes over a three-month shelf-period.

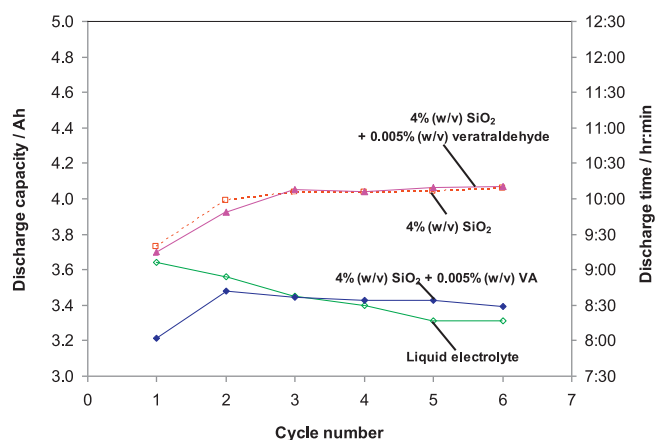


Fig. 8. Discharge capacities and discharge times of VRLA batteries prepared with different electrolytes during 100% DoD tests at a low-rate discharge (0.1 C) after a three-month shelf-period.

oxide sulfate hydrate that formed on the negative plate of the gel VRLA battery with VA may account for their observed lower remaining capacity and discharge capacity compared to those without any additive or with 0.005% (w/v) veratraldehyde (Figs. 7 and 8).

The low remaining capacity and discharge capacity levels of the liquid VRLA battery after three months of storage may have been due to the more severe corrosion of the electrodes in the liquid electrolyte that then led to the degradation of the electrode materials and, in turn, a loss in the ability to retain the battery capacity. In addition, oxygen generated as the corrosion by-product on the positive plates can come into contact and react with the negative plates leading to an increase in the self-discharge rate. The corrosion level was expected to be much more moderate in the gelled electrolytes, explaining why the electrodes of the gel VRLA batteries retained most of their capacities for up to five weeks after being manufactured. Similar to the fresh gel VRLA batteries (Fig. 3), the discharge capacities of the gel VRLA batteries after a three-month shelf-period were initially lower and then gradually increased with increasing discharge cycles (Fig. 8), except that for the gel VRLA battery prepared with 0.005% (w/v) VA, which showed a steady decrease after two cycles. These results indicated that the gel VRLA batteries with or without 0.005% (w/v) veratraldehyde retained their battery performance even after three months of storage. In contrast, despite its good initial performance (Fig. 3c), the gel VRLA battery with 0.005% (w/v) VA had a poor performance after being shelved for three months.

4. Conclusions

The influence of the SiO₂ concentration and the inclusion of the additives PMMA, PPY, PAM and VA on the gelling process, electrochemical behavior and battery performance under 100% DoD were investigated. Increasing the SiO₂ concentration led to faster gelling times and firmer gels. The additives differentially affected the gelling process, electrochemical behavior and battery

performance. PMMA and PPY did not significantly affect the gelling process, but PAM and VA led to a faster gelling time and a firmer gel. Overall, all the additives studied did not alter the main reaction of the lead-acid batteries, but VA tended to suppress the hydrogen evolution reaction. VA at 0.005% (w/v) enhanced the gel VRLA battery performance, which was potentially mediated via inhibition of the hydrogen evolution rate and/or the improved negative electrode. However, when the gel VRLA battery with 0.005% (w/v) VA was shelved for three months its discharge capacity dropped significantly to a much lower level than that without additive.

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